

STABILIZER FOR ELECTROLESS COPPER PLATING SOLUTION**FIELD OF THE INVENTION**

5 This invention relates to an improved electroless copper plating solution for plating non-conductive surfaces, such as through holes in multi-layered printed circuit boards. The improved electroless copper plating solution contains a formate stabilizer to prevent autodecomposition of copper from the plating solution.

BACKGROUND OF THE INVENTION

10 The electroless deposition of copper (here used to include copper alloys or intermetallics), i.e., the chemical plating of copper onto a catalytically active substrate surface by chemical reduction without the need for externally-applied electrical current, is a well-known process in extensive commercial use, particularly in the manufacture of printed circuit boards. Typically, electroless copper depositing baths are aqueous solutions
15 containing a bath-soluble source of copper, a reducing agent for the copper ion, a complexing agent for the copper, and a source, if necessary, of acid or alkali to achieve the pH at which the bath is intended to operate. The baths may also include a stabilizer. Typical baths are based upon formaldehyde (or a precursor thereof) as the reducing agent, although other reducing agents, such as hypophosphite may also be used. See, e.g., U.S.
20 Patent No. 4,279,948 to Kukanskis et al., the subject matter of which is herein incorporated by reference in its entirety.

Substrate surfaces to be electrolessly copper plated are clean, catalytically active surfaces. Typically, catalytic activation is by means of palladium/tin sols or solutions (see,
25 e.g., U.S. Pat. Nos. 3,011,920 and 3,532,518, the subject matter of which is herein incorporated by reference in its entirety) which often require an acceleration step to expose and/or activate the catalytic species. See, e.g., U.S. Pat. No. 4,608,275 to Kukanskis, the subject matter of which is herein incorporated by reference in its entirety.

30 Among the most important uses of electroless copper plating is in providing the requisite conductive metal surface in the through-holes which are provided in double-sided and multilayer printed circuits and through which conductive interconnection is achieved between or among circuit patterns on the opposed substrate and/or innerlayer surfaces. The

integrity of the conductive metal layer provided on these through-hole surfaces, in terms of its full coverage, adherence, and resistance to cracking or peeling under stress (particularly as will occur when components are later soldered to the printed circuit), is of critical importance in achieving useful printed circuit boards.

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One type of commercially satisfactory electroless copper bath uses formaldehyde-type reducing agents and operate at high pH levels (11-13). These baths are inherently unstable over long periods of use and/or at elevated temperatures. Electroless copper plating baths of this type are prone to bath instability, particularly at operating
10 temperatures above 120 °F. Higher temperatures release dissolved oxygen, a primary electroless copper stabilizer, from the plating solution. A low dissolved oxygen content allows copper ions to shift between the +1 and +2 valence state, resulting in the spontaneous reduction of copper ions to metal. The metal may then catalyze additional copper reduction and result in run-away plating in the tank.

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The baths generally require the incorporation of "catalytic poisons" in carefully controlled trace amount to avoid spontaneous (bulk) decomposition. The plating bath must therefore always operate in a relatively narrow range between conditions which are conducive to satisfactory deposition on controlled areas of a substrate on the one hand, and
20 random, unwanted, copper plate-out on tank walls, racks, etc., on the other.

To prevent the spontaneous decomposition of the plating bath composition and thus prevent the valence shift in copper in the plating bath composition, stabilizers can be added to the plating solution. Examples of stabilizers that have been suggested for use in
25 electroless copper plating solutions include cyanide and surfactants such as polyethyleneglycolstearylamine (U.S. Pat. No. 3,804,638), polyethylene oxide, polyethylene glycol, polyether, polyester, etc.

Choosing a proper stabilizer is essential to proper operation of the plating bath. In
30 some instances, the stabilizer is prone to absorption onto the surface of plating film, disturbing deposition of copper and retarding the plating rate. Thus, development of techniques satisfying the plating rate, mechanical strength of plating film, and stability of plating solution at the same time has been in keen demand.

SUMMARY OF THE INVENTION

The invention relates to the discovery that the addition of a formate salt or formic acid to a traditional formaldehyde-type electroless copper plating solution provides increased stability at elevated operating conditions.

The improved electroless copper plating bath composition of the invention generally comprises:

- a source of copper;
- 10 - a reducing agent;
- a complexing agent;
- a pH adjuster; and
- a stabilizer selected from the group consisting of formic acid and formate salts.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The inventor has surprisingly discovered that the addition of a formate salt or neutralized? formic acid to a traditional formaldehyde-type electroless copper plating bath composition can provide bath stability at the elevated temperatures required for plating, preferably temperatures above 120°F. A preferred formate salt is sodium formate.

While the mechanism of stability is not currently known, it is theorized that the formate may complex the copper, preventing the valence shift from +1 to +2 or that the reaction product of formaldehyde oxidation shifts the reaction equilibrium back towards the reactants.

The copper source in the plating solution may be comprised of any available bath soluble copper salt. Copper chloride and copper sulfate are generally preferred because of availability, but nitrate, other halide, or organic copper compounds such as acetates can also be used.

The preferred reducing agent for the plating solution is formaldehyde or a formaldehyde precursor. Suitable formaldehyde precursors for use in electroless copper plating baths would generally be known to one skilled in the art. Hypophosphites may also be used.

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Proper pH level of the copper bath is important to the operability of the plating bath. In formaldehyde-type electroless copper plating baths of the invention, the pH is normally maintained in the alkaline range, generally between 11 and 13. If adjustment of pH is needed, any standard base may be employed to return the level to correct operating range. Commonly used pH adjusters include sodium hydroxide and potassium hydroxide.

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Effective complexing agents include N-hydroxyethyl ethylenediamine triacetic acid (HEEDTA), ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and alkali metal salts of these. Tartates and salts of therefore are also used.

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The plating composition is preferably subjected to air agitation during use. Plating time may range from about a few minutes to several hours depending upon the thickness required.

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EXAMPLE 1

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A standard copper plating bath is made up as follows:

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Copper Sulfate	4g/l copper
Formaldehyde	5 g/l
Ethylenediaminetetraacetic acid (EDTA)	50g/l
Sodium Hydroxide	20g/l
2,2,-bipyridine	5 ppm

Even with air agitation, the plating solution starts to form copper in solution when the composition is heated to between 155 and 160°F for one hour.

EXAMPLE 2

- 5 The same copper plating bath solution as in Example 1 was prepared, except that 10 grams/liter of sodium formate was added to the bath composition. The plating solution remained stable at temperatures between 155 and 160°F, even when air agitation was interrupted for short periods of time.